



Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis

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ABSTRACT

In recent years, torrefaction, a mild pyrolysis process carried out at the temperature range of 200–300 °C, has been considered as an effective route for improving the properties of biomass. Hemicellulose, cellulose, lignin and xylan are the basic constituents in biomass and their thermal behavior is highly related to biomass degradation in a high-temperature environment. In order to provide a useful insight into biomass torrefaction, this study develops the isothermal kinetics to predict the thermal decompositions of hemicellulose, cellulose, lignin and xylan. A thermogravimetry is used to perform torrefaction and five torrefaction temperatures of 200, 225, 250, 275 and 300 °C with 1 h heating duration are taken into account. From the analyses, the recommended values of the order of reaction of hemicellulose, cellulose, lignin and xylan are 3, 1, 1 and 9, respectively, whereas their activation energies are 187.06, 124.42, 37.58 and 67.83 kJ mol⁻¹, respectively. A comparison between the predictions and the experiments suggests that the developed model can provide a good evaluation on the thermal degradations of the constituents, except for cellulose at 300 °C and hemicellulose at 275 °C. Eventually, co-torrefaction of hemicellulose, cellulose and lignin based on the model is predicted and compared to the thermogravimetric analysis.

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1. Introduction

Fossil fuels play the most important role in energy market over the past several decades, and until now they are still the most important merchants for energy supply. However, fossil fuels are being consumed rapidly so that their reserves are reduced in a significant way. Meanwhile, the mass consumption of fossil fuels has induced a number of environmental problems, such as air pollution, acid rain and atmospheric greenhouse effect or global warming [1]. By virtue of great concerns on the depletion of non-renewable energy resources and environmental problems, the development of renewable energy and alternative fuel for environmental sustainability has become a crucial topic currently. Among developing renewable energies, bioenergy is one of the most important energy resources so far in that biomass is available all over the world and it has been extensively employed in underdeveloped, developing and developed countries [2,3].

Biomass can be utilized in the forms of solid, liquid and gas for energy. Solid biomass can be combusted directly or blended with coal for the purpose of getting heat and power [4]. Liquid fuels, say,

biooil, biodiesel and bioethanol, can be obtained from biomass through thermal, chemical and biological conversions [5–7]. Gas fuels or synthesis gas, namely, syngas, can be produced from biomass via the process of gasification [8]. Generally speaking, biomass is characterized by its high moisture content, low calorific value, hygroscopic nature and larger volume or low bulk density. This results in low conversion efficiency and grindability as well as difficulty of storage of biomass [9]. In the past, a number of methods of pretreatment have been developed to improve conversion efficiency; one of the methods for solid biomass is torrefaction.

Torrefaction is a mild pyrolysis process carried out at temperatures ranging from 200 to 300 °C in an inert atmosphere or nitrogen environment [9,10]. In this process, in addition to moisture removal, the lignocellulosic structure of biomass is thermally degraded in part, especially for the reactive hemicellulose fraction [11]. Reviewing recent studies of torrefaction, it has been verified that torrefied biomass has the following properties: (1) the moisture content of raw biomass drops drastically [12]; (2) the O/C ratio of the torrefied biomass is decreased [13,14]; (3) the grinding energy of the pretreated biomass is lower [9]; and (4) the hygroscopic nature featured by raw biomass is transformed to be hydrophobic [15]. As a result, the advantages accompanied by torrefaction include: (1) the energy density of the torrefied biomass is increased [16]; (2) the ignitability, reactivity and grindability of the biomass are improved

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Nomenclature

A	Pre-exponential factor (min^{-1})
E_a	Activation energy (kJ mol^{-1})
k	Rate constant (min^{-1})
n	Order of reaction ($-$)
R	Universal gas constant ($=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	Temperature (K)
t	Heating time (min)
X	Conversion of sample ($-$)
W	Weight of tested sample (mg)

Subscript

0	Beginning of torrefaction
i	Initial state (at 105°C)
f	Final state (at 800°C)

[17,18]; (3) the biological resistance to the decay of the torrefied biomass is enhanced [14]; and (4) the storage, transport and delivery of the torrefied biomass is easier in contrast to its parent biomass [9]. Besides, the contents of constituents inside various biomasses are different each other; torrefaction will lead to more uniform contents of the constituents. Because the temperatures of torrefaction are not high, it can be carried out through recovering waste heat in industries rather than providing extra energy for heating. The waste heat can be obtained from boilers, reheating furnaces or flue gases. Accordingly, torrefaction can also improve the energy efficiency of the industrial process.

Regarding the applications of torrefaction, the study of Phanphanich and Mani [9] has reported that torrefaction could improve grinding properties of biomass and make the fuel characteristics, such as fixed carbon and heating value, closer to coal. If biomass is grinded into powder, it can be blended with coal to serve as a pulverized fuel [4]. However, the hygroscopic behavior and higher volatile matter contained in the biomass powder make the difficulty of blending encountered. In this aspect, torrefied biomass with hydrophobic feature has higher porosity and greater reactivity during combustion and gasification. Therefore, Deng et al. [15] addressed that the torrefaction process was a promising pretreatment method for agricultural residues to combine with coal for co-gasification. In the analysis of Uslu et al. [19], they pointed out that torrefaction in combination with a pelletization process was more advantageous than the pelletization process alone.

In reviewing recent research of torrefaction, it can be found that most of the studies are focused on the weight loss, elemental analysis, grindability and heating value of biomass from torrefaction [3,11,20], the effect of torrefaction conditions on the physical and chemical properties of biomass [13,21] and the economic evaluation of biomass torrefaction [19]. Meanwhile, the study of torrefaction kinetics has been carried out by Prins et al. [11], Rousset et al. [22], Turner et al. [23] and Repellin et al. [24] to aid in predicting the weight loss process of biomass. Instead of the study of kinetics of specified biomass, the present study is intended to analyze the thermal decompositions of main constituents of biomass, namely, hemicellulose, cellulose and lignin, in a torrefaction environment using a thermogravimetry (TG). It is known that xylan is a reactive constituent contained in hemicellulose and hemicellulose plays a vital role in the thermal degradation of biomass in a torrefaction environment [11]. Therefore, the isothermal kinetics describing the thermal degradations of the four basic constituents is developed in this study. Moreover, co-torrefaction behavior predicted based on the conducted kinetics will also be compared to the experimental measurements.

2. Torrefaction kinetics

Basically, torrefaction is an isothermal pretreatment process so that the torrefaction kinetics can be established based on isothermal degradation of biomass. Typically, the rate of reaction of a sample is given by the following equation [25,26]:

$$\frac{dX}{dt} = k(1 - X)^n \quad (1)$$

where X is the conversion of the sample and it is defined by

$$X = \frac{W_i - W}{W_i - W_f} \quad (2)$$

In the foregoing equation, W is the weight of the sample at time t , W_i the initial weight of the sample and W_f the final weight of the sample. At present, to provide a standard of analysis, the initial and final weights are identified at 105 and 800°C , respectively. If the order of reaction is unity (i.e. $n = 1$), the integration of Eq. (1) in the course of torrefaction gives

$$\ln \left(\frac{1 - X_0}{1 - X} \right) = k(t - t_0) \quad \text{for } n = 1 \quad (3)$$

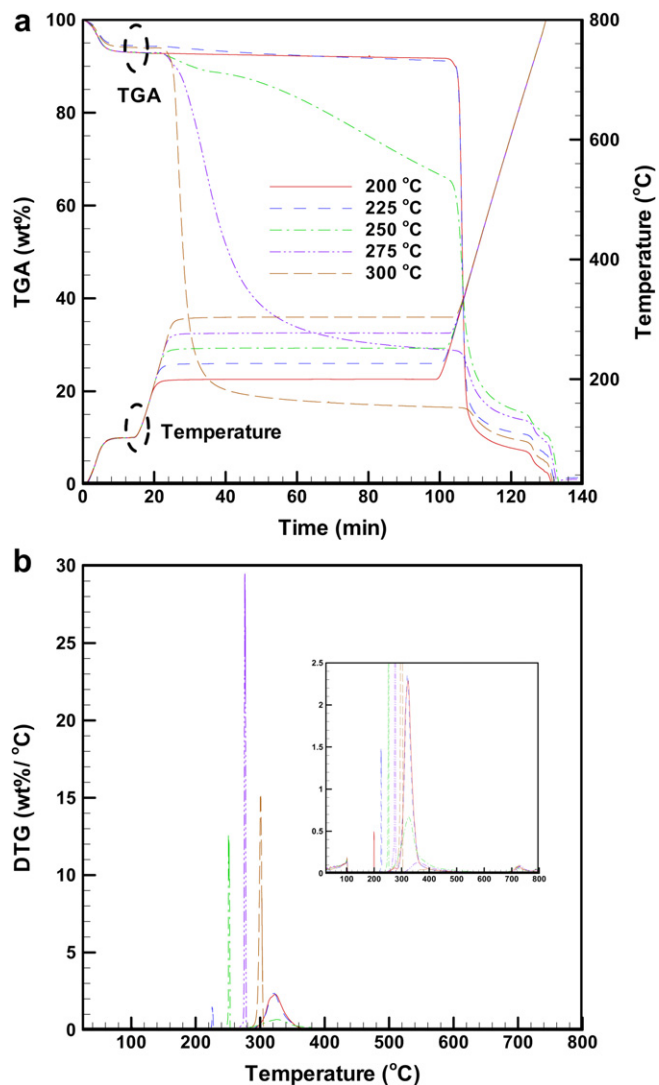


Fig. 1. Distributions of (a) TGA and (b) DTG of hemicellulose at five different torrefaction temperatures.

X_0 is the conversion of the sample at the beginning of torrefaction where $t = t_0$. Eq. (3) implies that the plot of $\ln(1-x)^{-1}$ versus torrefaction time $t-t_0$ gives a straight line with the slope equal to the rate constant k . Therefore, for a given material at various torrefaction temperatures, a set of data of rate constant can be obtained. On the other hand, if the order of reaction is not unity, the integration of Eq. (1) becomes

$$(1-X)^{1-n} - (1-X_0)^{1-n} = k(n-1)(t-t_0) \text{ for } n \neq 1 \quad (4)$$

Similarly, the plot of $(1-X)^{1-n}$ versus torrefaction time gives a straight line with the slope equal to $(n-1)k$. Accordingly, the rate constants of the sample at various torrefaction temperatures are obtained.

Normally, the dependence of rate constant on temperature is assumed to obey Arrhenius law, that is

$$k = A \exp\left(\frac{-Ea}{RT}\right) \quad (5)$$

The logarithmic form of Eq. (5) gives

$$\ln(k) = \ln(A) - Ea/RT \quad (6)$$

From the obtained rate constants corresponding to various torrefaction temperatures, if the plot $\ln(k)$ versus T^{-1} is featured by a straight line, the slope of the line is equal to $-Ea/R$ and the intercept is equal to $\ln(A)$. As a consequence, the activation energy and pre-exponential factor in the kinetics of torrefaction are obtained.

3. Experimental

In this study, four basic constituents in biomass, including hemicellulose, cellulose, lignin, and xylan, are chosen as the tested materials to be torrefied. Hemicellulose and xylan came from SIGMA with the product numbers of H2125-150KU and X-4252, respectively. Cellulose was purchased from Alfa Aesar with the product number of A17730. Lignin was obtained from Tokyo Chemical Industrial Co. and its product number was L0045. Thermogravimetric analysis (TGA, PerkinElmer Diamond TG/DTA) was selected to perform the torrefaction processes of the four materials. In each test when a material was measured, around 5 mg of sample was loaded in a crucible and it was mounted in the heating chamber of the thermogravimetry (TG). N_2 was used as a carrier gas and transported into the TG so that the material was torrefied in an inert environment without oxidant. The flow rate of the carrier gas

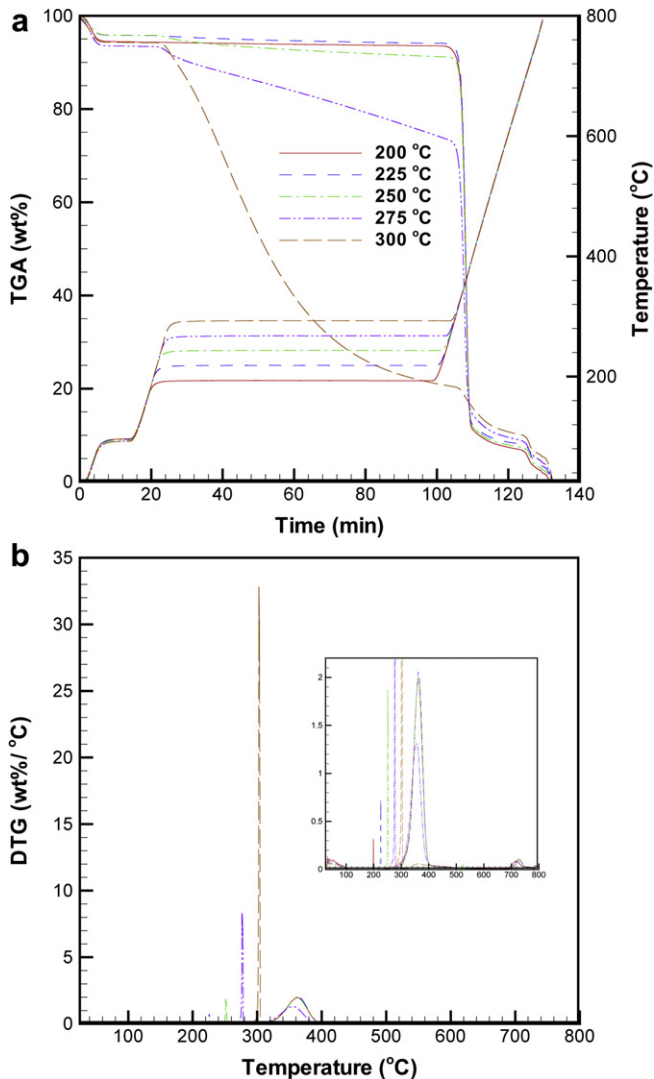


Fig. 2. Distributions of (a) TGA and (b) DTG of cellulose at five different torrefaction temperatures.

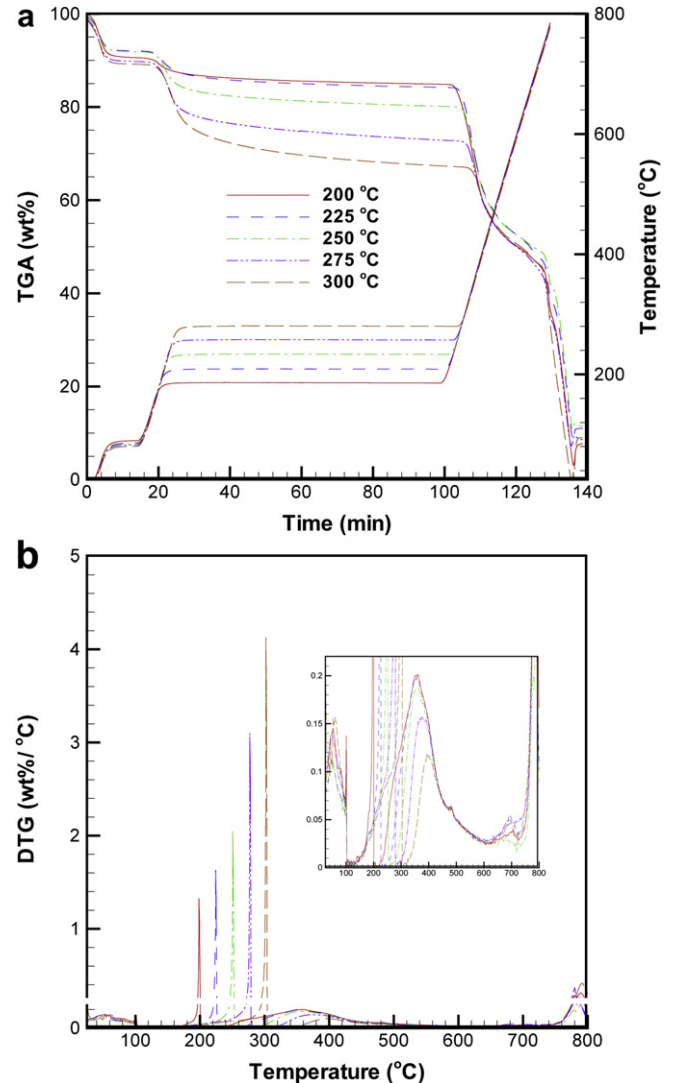


Fig. 3. Distributions of (a) TGA and (b) DTG of lignin at five different torrefaction temperatures.

was fixed at 200 cc min^{-1} (at 25°C and 1 atm). When the torrefaction process of a sample was executed, the entire experimental process was divided into three dynamic and two isothermal heating periods. Specifically, the sample was heated to 105°C from room temperature with the heating rate of $20^\circ\text{C min}^{-1}$, followed by maintaining the sample at 105°C for 10 min to ensure completely removing the moisture of the sample. Afterward, the sample was heated to the specified torrefaction temperature with the heating rate of $20^\circ\text{C min}^{-1}$ again. Once the torrefaction temperature was reached, the material was torrefied for 1 h. Then, it was pyrolyzed with the heating rate of $20^\circ\text{C min}^{-1}$ until the temperature of 800°C was attained. Co-torrefactions of hemicellulose, cellulose and lignin (weight ratio 1:1:1) at various torrefaction temperatures for 1 h were also carried out. In the course of experiment, the instantaneous weight of the sample was measured and recorded at a frequency of 2 Hz. To ensure the measured quality of the study, the TG was periodically calibrated and the details of calibration can be found elsewhere [3].

4. Results and discussion

As mentioned earlier, torrefaction is a thermal pretreatment process for the temperature range of $200\text{--}300^\circ\text{C}$. Therefore, five

different torrefaction temperatures of 200 , 225 , 250 , 275 and 300°C are taken into account and the torrefaction duration is fixed at 1 h.

4.1. Torrefaction behavior

The distributions of TGA and derivative thermogravimetric (DTG) analysis of hemicellulose, cellulose, lignin and xylan are displayed in Figs. 1–4, respectively. Considering the reaction of hemicellulose, Fig. 1a clearly indicates that the torrefaction temperatures of 200 and 225°C almost play no part in thermal degradation of hemicellulose in that the weight decrements of the sample in the course of torrefactions are 0.8 and $2.3 \text{ wt\%}$, respectively. With the temperature of 250°C , the weight loss from the torrefaction is $19.5 \text{ wt\%}$, revealing that the influence of the pretreatment becomes important. In fact, the impact of the torrefaction can also be identified from the distribution of DTG (Fig. 1b) where the peak at 250°C is much larger than those at 200 and

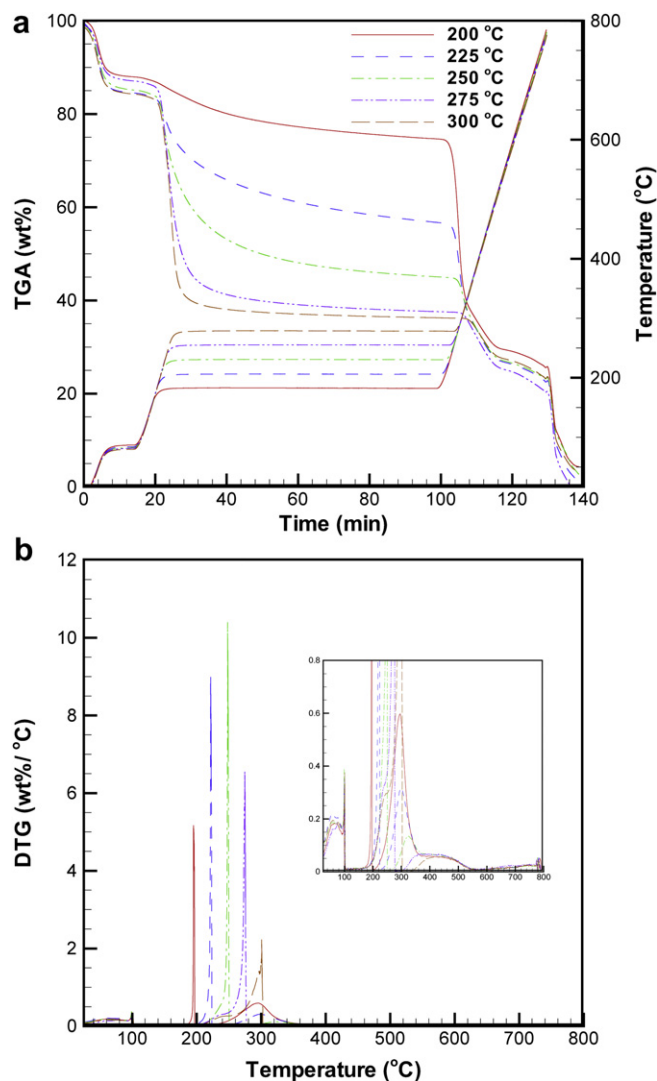


Fig. 4. Distributions of (a) TGA and (b) DTG of xylan at five different torrefaction temperatures.

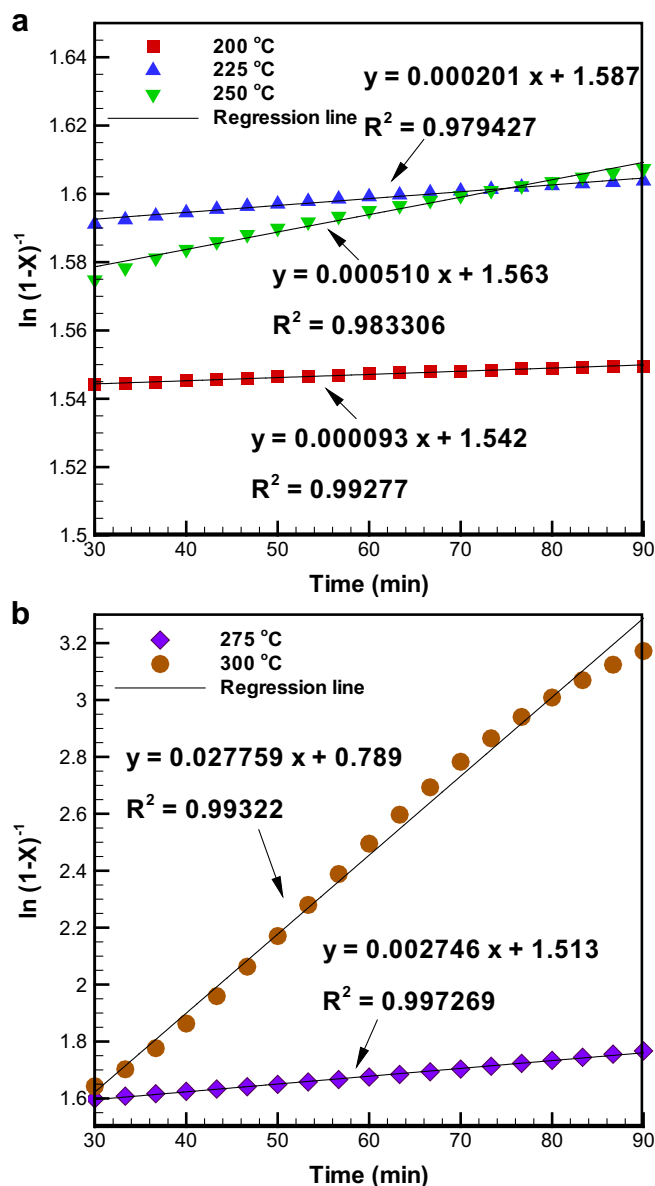


Fig. 5. Plot of cellulose conversion with respect to torrefaction time at (a) 200 , 225 and 250°C as well as (b) 275 and 300°C during the torrefaction period.

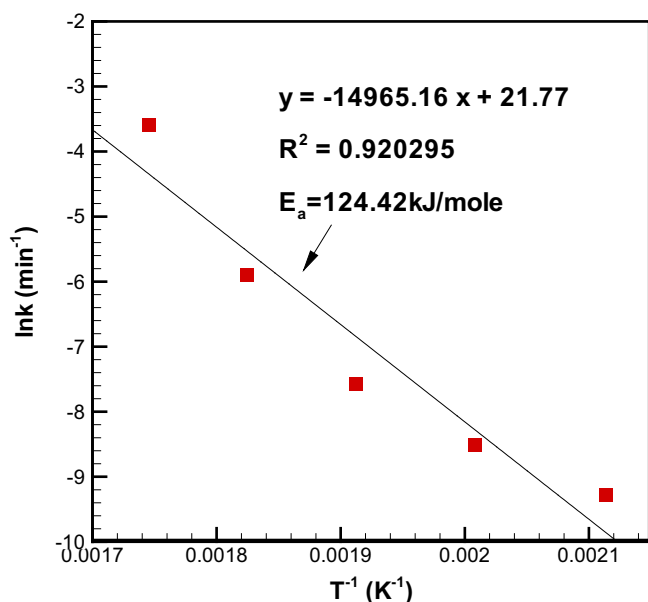


Fig. 6. Plot of reaction rate constant with respect to torrefaction temperature of cellulose.

225 °C. For the torrefaction temperature of 275 °C, 52.6 wt% of hemicellulose is lost. When the temperature is lifted to 300 °C, only 16.8 wt% of hemicellulose is consumed from the torrefaction, arising from the fact that a large portion of hemicellulose has been depleted before 300 °C. For this reason, the DTG curve at 300 °C is not as high as that at 275 °C. Behind the torrefaction peaks, pyrolysis peaks occur at around 320–325 °C. The torrefaction peaks of hemicellulose are exothermic in nature, whereas the pyrolysis peaks are endothermic [11].

When attention is paid to cellulose, Fig. 2a depicts that the thermal degradation of cellulose is slight if the torrefaction temperature is less than or equal to 250 °C. For instance, corresponding to the torrefaction temperatures of 200, 225 and 250 °C, the weight losses of cellulose are 0.5, 1.2 and 3.0 wt%, respectively.

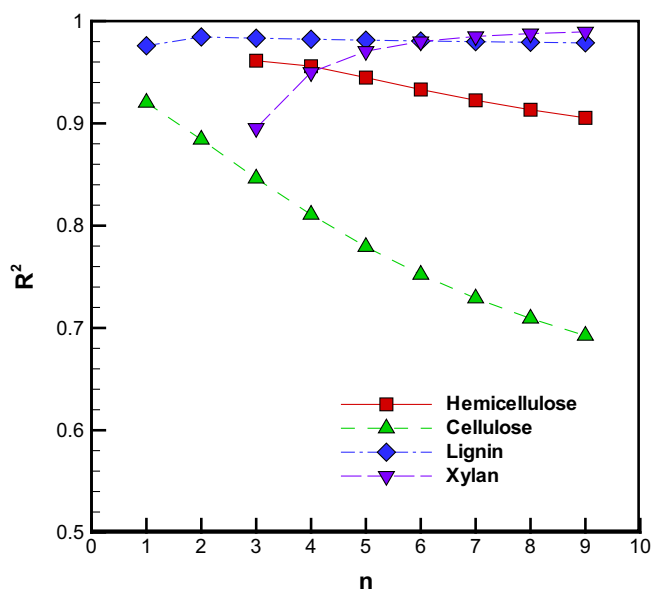


Fig. 7. Distributions of R^2 of regression line versus order of reaction of hemicellulose, cellulose, lignin and xylan.

Table 1

Summary of activation energies and pre-exponential factor of the hemicelluloses, cellulose, xylan and lignin.

Material	Temperature (°C)	n^a (–)	E_a^b (kJ mol ^{–1})	A^c (min ^{–1})	Reference
Hemicellulose	200–350 ^d	1	127	9.5×10^{10}	[28]
	230–340 ^d	1.7	163	3.98×10^{14}	[29]
	340–390 ^d	1.8	175	3.16×10^{14}	[29]
	200–300 ^e	3	187.06	4.13×10^{16}	Present study
Cellulose	200–270 ^d	0.8	93	3.16×10^8	[29]
	253–394 ^d	1	278.5	3.63×10^{19}	[30]
	230–380 ^d	1	185	–	[31]
	300–340 ^d	1	227.02	3.36×10^{18}	[32]
	200–300 ^e	1	124.42	2.86×10^9	Present study
Lignin	226–435 ^d	0.5	39.4	–	[33]
	220–380 ^d	1	7.8	2.96×10^{-3}	[32]
	283–441 ^d	1	30.7	8×10^{-4}	[30]
	320–390 ^d	1.4	105	1.58×10^8	[30]
	200–300 ^e	1	37.58	6.625	Present study
Xylan	182–315 ^d	1	137.9	2.28×10^7	[30]
	200–400 ^d	1	193	6×10^{18}	[34]
	220–300 ^d	1	69	1.25×10^5	[32]
	200–300 ^e	9	252.28	7.28×10^{25}	Present study

^a Order of reaction.

^b Activation energy.

^c Pre-exponential factor.

^d Non-isothermal kinetics.

^e Isothermal kinetics.

Behind the torrefactions the pyrolysis peaks are exhibited at around 355–360 °C which are intrinsically endothermic [11,27]. When cellulose is torrefied at 275 °C, it is noted that the decrement in sample weight is linearly proportional to the torrefaction duration. This reflects that the torrefaction period plays an important role in thermal decomposition of cellulose at 275 °C. In comparison to the DTG peaks of 200, 225 and 250 °C, Fig. 2b indicates that the DTG peak at 275 °C grows markedly. When cellulose is torrefied at 300 °C, its weight drops rapidly with time. Meanwhile, a sharp DTG distribution during torrefaction is apparently exhibited and the

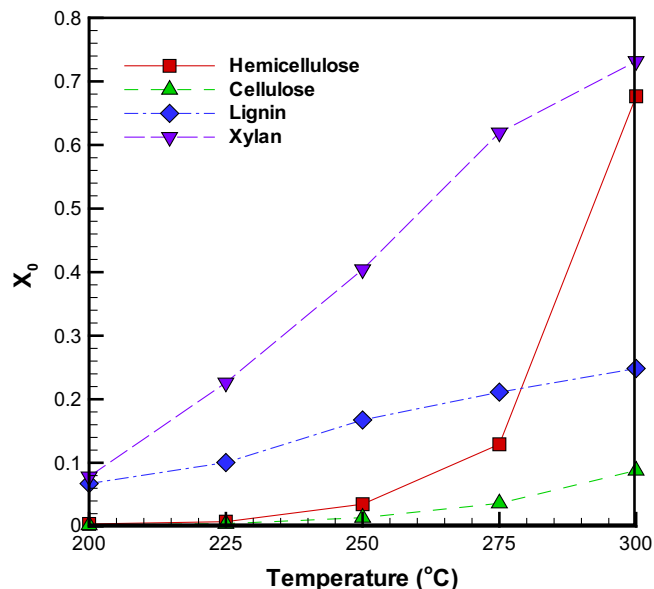


Fig. 8. Distributions of conversion of hemicellulose, cellulose, lignin and xylan at the beginning of torrefaction at various torrefaction temperatures.

pyrolysis peak behind the torrefaction disappears, as shown in the embedded small figure. These phenomena reveal that the torrefaction at 300 °C influences the structure of cellulose profoundly.

With emphasis shifted to lignin, Fig. 3 suggests that the resistance of lignin against the torrefaction is notable, stemming from the relatively low weight loss (Fig. 3a). For instance, even though the torrefaction temperature is as high as 300 °C, only 7.4 wt% of lignin is pyrolyzed from the torrefaction. In view of the characteristic stated above, it can be seen that the intensities of DTG peaks shown in Fig. 3b are much small compared to those shown in Figs. 1b and 2b. For the torrefaction temperatures of 250, 275 and 300 °C, the TGA curves also indicate that the longer the torrefaction duration, the more pronounced the weight loss. On the other hand, it is noteworthy that the structure of lignin is still affected by the torrefactions to a certain extent, as a result of shift rightward of the pyrolysis peak with increasing torrefaction temperature. Specifically, corresponding to the torrefaction temperatures of 200, 225, 250, 275 and 300 °C, the pyrolysis peak temperatures occur at 355, 355, 360, 378 and 396 °C, respectively.

Upon inspection of the thermal decomposition of xylan shown in Fig. 4a, it is a reactive constituent so that its weight drops at

200 °C is relatively drastic compared with those shown in Figs. 1–3. Meanwhile, Fig. 4b shows that the torrefaction process at 250 °C has a maximum impact on the thermal degradation of xylan since the weight loss is 14.6%. In contrast, the weight losses at 275 and 300 °C are 8.0 and 3.5%, respectively, implying that the torrefaction temperature of 250 °C is sufficiently high to decompose xylan. Because of this, the peaks of DTG curves at 275 and 300 °C are not as high as that at 250 °C. Fig. 4 also suggests that the torrefaction processes at 200, 225 and 250 °C are sensitive to torrefaction duration, whereas the effect of duration on weight loss at 275 and 300 °C is relatively slight. As mentioned earlier, xylan is a reactive constituent contained in hemicellulose. A comparison between Figs. 1a and 4a indicates that the reactivity of xylan is higher than that of hemicellulose in that the TGA curves of the former drop faster than those of the latter. In addition, the DTG peak at the torrefaction temperature of 200 °C can be found in Fig. 4b, whereas it can't be found in Fig. 1b.

In the study of Prins et al. [11], it has been reported that hemicellulose decomposed at temperature in the range of 225–325 °C, cellulose at 305–375 °C and lignin gradually over the temperature

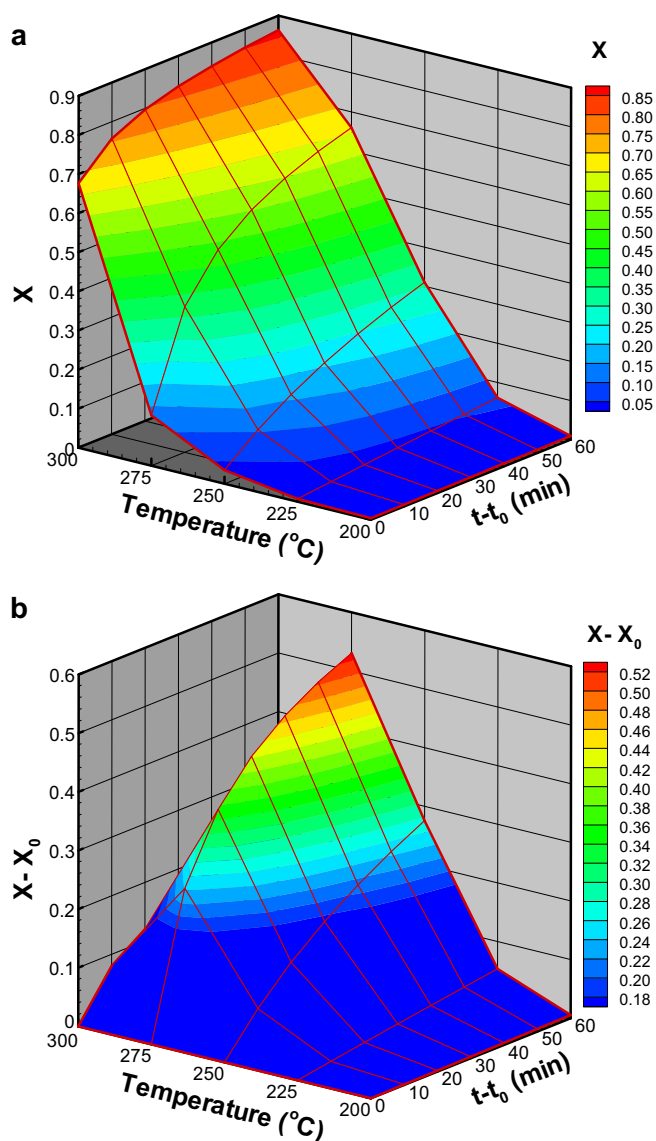


Fig. 9. Three-dimensional profiles of (a) conversion and (b) increment of conversion of hemicellulose.

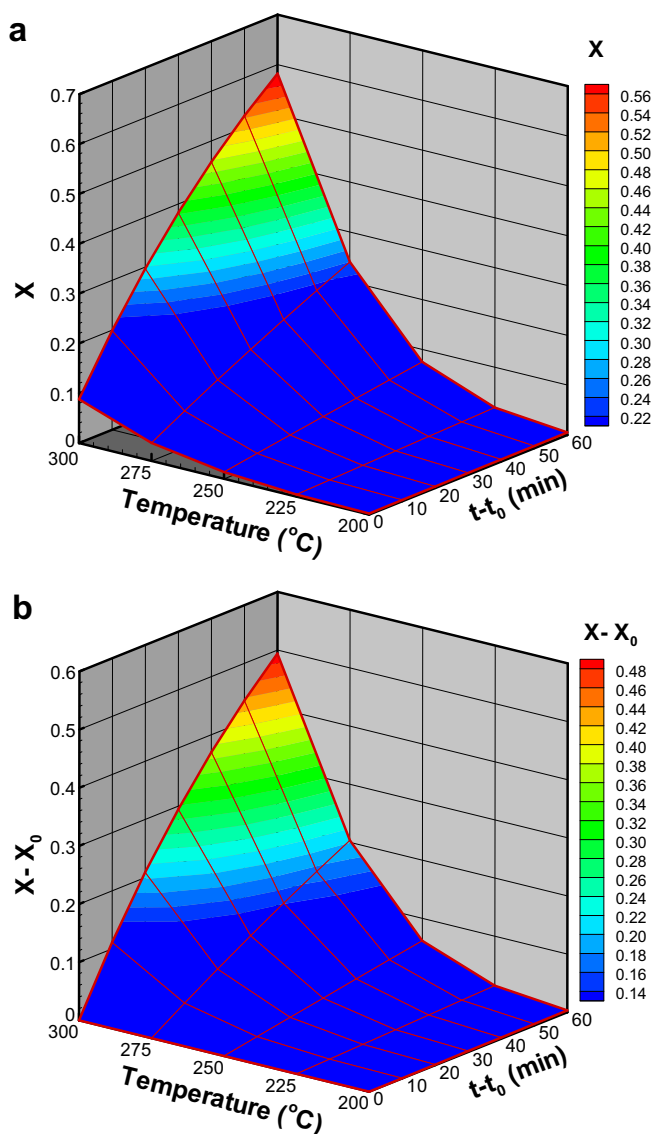


Fig. 10. Three-dimensional profiles of (a) conversion and (b) increment of conversion of cellulose.

range of 250–500 °C. From the pyrolysis peaks shown in Figs. 1–4, they are located within the same temperature ranges. Consequently, the obtained results in the current study are consistent with the illustrations of Prins et al. [17].

4.2. Torrefaction kinetics

If the order of reaction of a material is unity, the plot of $\ln(1-x)^{-1}$ versus torrefaction time will give a straight line with the slope equal to the rate constant k , as expressed in Eq. (3). Alternatively, if the order of reaction is not unity, Eq. (4) will be invoked to get the rate constant by plotting $(1-x)^{1-n}$ versus torrefaction time. Fig. 5 demonstrates the plots of cellulose at the five torrefaction temperatures with the condition of $n = 1$. The distributions indicate that the values of R^2 of the regression lines are always larger than 0.98, reflecting that $n = 1$ is an appropriate value to approach the rate constant of cellulose. Based on these regression lines, five rate constants corresponding to the five torrefaction temperatures are sketched in Fig. 6. Furthermore, when $\ln(k)$ with respect to T^{-1} is plotted, Fig. 6 depicts that the regression line is also

characterized by a strongly linear relationship in that the value of R^2 is larger than 0.92. As a result, the activation energy of the isothermal torrefaction kinetics of cellulose is 124.42 kJ mol⁻¹.

To obtain the appropriate values of the order of reaction of the four basic constituents, the distributions of R^2 at various values of n in accordance with the plot of $\ln(k)$ with respect to T^{-1} are profiled in Fig. 7. For hemicellulose and xylan, the analyses suggest that the linear relationship between the reaction rate constant and torrefaction temperature is not exhibited if n is less than 3, implying that the activation energy and chemical kinetics are unable to be obtained. Hence, only the values for $n \geq 3$ are displayed. It can be seen that the values of R^2 of hemicellulose, cellulose and xylan are sensitive to n ; alternatively, it is almost invariant for lignin. Accordingly, the recommended values of n for establishing isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan are 3, 1, 1 and 9, respectively. The values of activation energy, pre-exponential factor and the order of reaction in the chemical kinetics of the four constituents from the present study are tabulated in Table 1. It can be found that the activation energies of hemicellulose, cellulose, lignin and xylan are 187.06, 124.42,

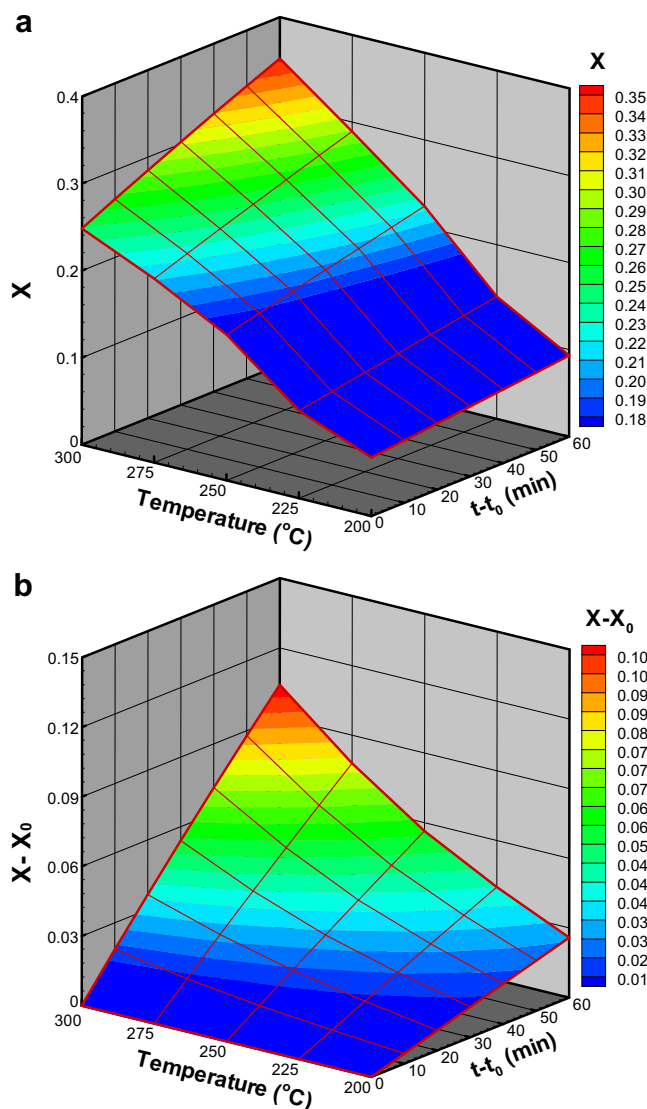


Fig. 11. Three-dimensional profiles of (a) conversion and (b) increment of conversion of lignin.

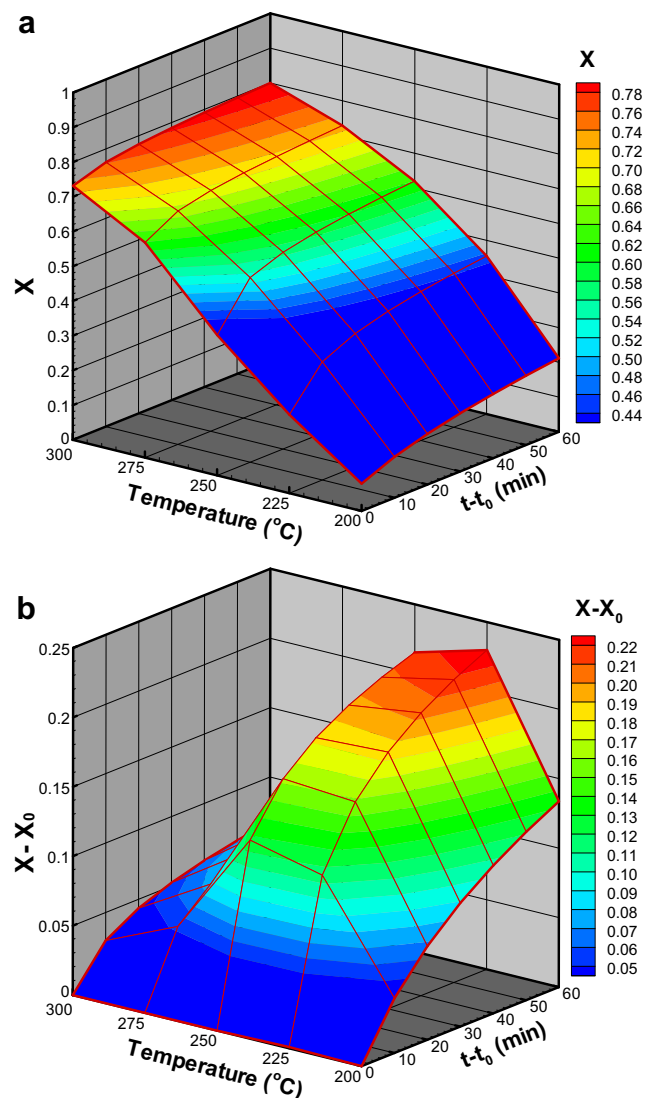


Fig. 12. Three-dimensional profiles of (a) conversion and (b) increment of conversion of xylan.

37.58 and 252.28 kJ mol⁻¹, respectively. The results from other studies are listed in the table as well. Overall, the obtained results in the present study are in reasonable ranges when compared to other studies. However, it should be emphasized the chemical kinetics in other studies was developed based on non-isothermal thermal degradation, whereas the currently obtained results pertain to isothermal kinetics.

4.3. Prediction of torrefaction process

Once the reaction rate constant is obtained, the conversion of a material at a certain instant can be evaluated from Eq. (3) or (4). For cellulose and lignin with $n = 1$, their conversion can be obtained from Eq. (3) and expressed as

$$X = 1 - (1 - X_0) \exp[-k(t - t_0)] \\ = 1 - (1 - X_0) \exp[-A(t - t_0) \exp(-Ea/RT)] \quad (7)$$

Alternatively, for hemicellulose and xylan, seeing that their values of n are not equal to unity, Eq. (4) is thus employed and their conversion is written as

$$X = 1 - \left[k(t - t_0)(n - 1) + (1 - X_0)^{1-n} \right]^{\frac{1}{1-n}} \\ = 1 - \left[A \exp\left(\frac{-Ea}{RT}\right) (t - t_0)(n - 1) + (1 - X_0)^{1-n} \right]^{\frac{1}{1-n}} \quad (8)$$

X_0 shown in Eqs. (7) and (8) stands for the conversion of the tested sample at the beginning of torrefaction. The profiles of X_0 of the four constituents are sketched in Fig. 8.

Based on the obtained n , A , Ea and X_0 , the predicted profiles of conversion and increment of conversion of the four constituents in the course of torrefaction are presented in Figs. 9–12. As far as hemicellulose is concerned, increasing torrefaction temperature leads to a substantial growth in X_0 ; it is especially pronounced as the torrefaction temperature increases from 250 to 300 °C (Fig. 9a). As a consequence, Fig. 9b suggests that the most violent increment in conversion is exhibited at the torrefaction temperature of 275 °C and the maximum increment is 53.1%. In regard to cellulose, its thermal degradation is apparently different from hemicellulose, that is, the higher the torrefaction temperature, the more drastic the impact of the torrefaction duration on conversion (Fig. 10). This

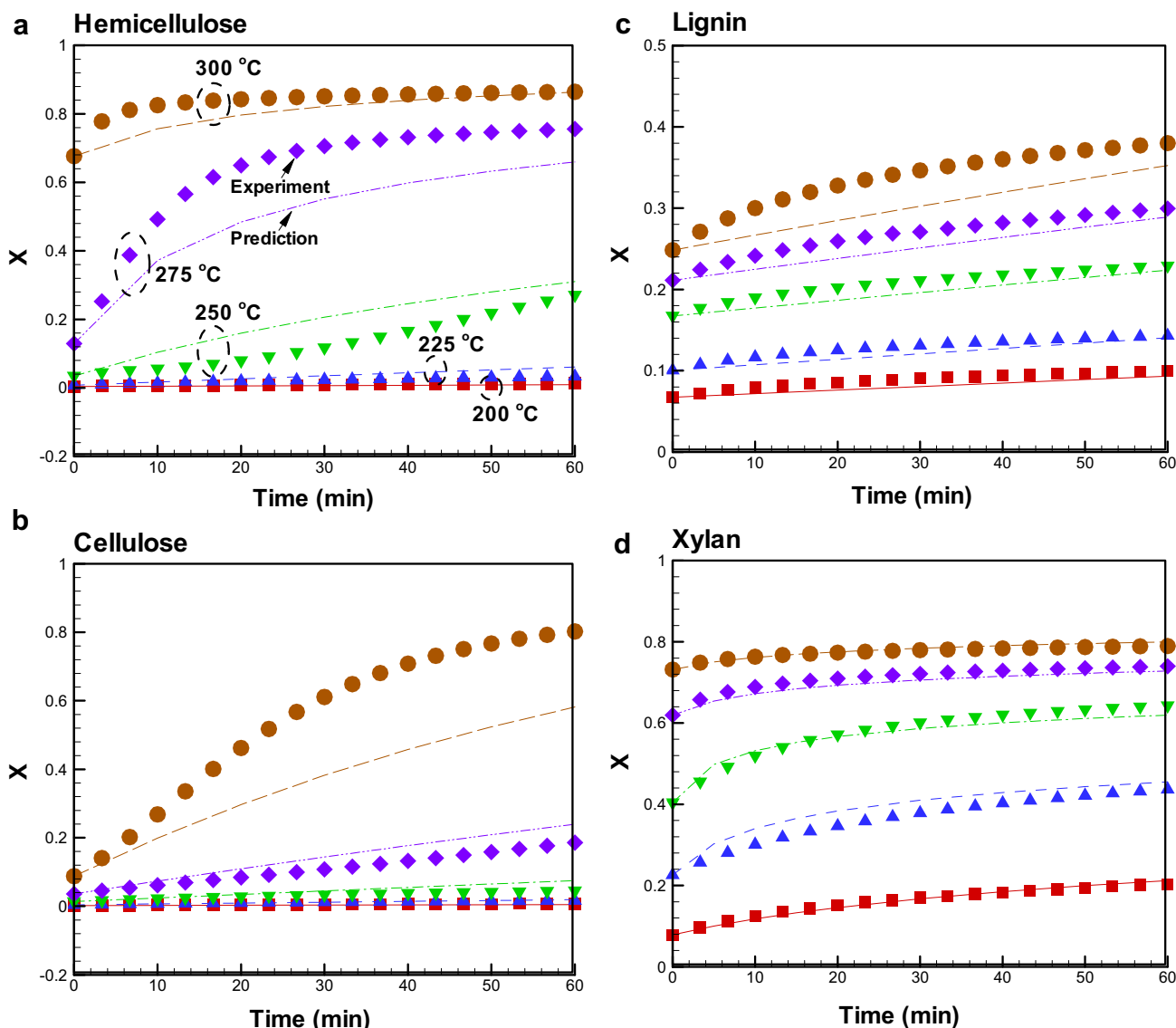


Fig. 13. Comparisons of conversion between predictions and experiments of (a) hemicellulose, (b) cellulose, (c) lignin and (d) xylan.

is the reason that the maximum increment of conversion is 49.4% which develops at 300 °C and 1 h. Considering lignin, unlike hemicellulose and cellulose, its increment in conversion is relatively slight, as a result of the maximum increment being 10.4% (Fig. 11b). In examining xylan, an obvious increment occurs at 225 and 250 °C (Fig. 12b) where the maximum increment is 23.0% at 225 °C and 1 h. This is attributed to the reactive nature of xylan. Before the TGA curve reaches the higher torrefaction temperatures such as 275 and 300 °C, a large portion of xylan has been depleted (Fig. 12a), thereby resulting in the relatively small increment of conversion with time.

4.4. Comparison between prediction and measurement

To evaluate the reliability of the torrefaction kinetics, comparisons between the predictions and experimental data are displayed in Fig. 13. When one is concerned with hemicellulose, it can be seen that the predictions are in good agreement with the experiments, except for 275 °C where the conversion is underestimated (Fig. 13a) and the maximum relative error between the prediction and the experiment is 34%. This is attributed to the intensified reaction of hemicellulose at the aforementioned temperature. In contrast, the model underestimates the conversion of cellulose at 300 °C where the reaction of cellulose is the most violent (Fig. 13b) and the maximum relative error is 37%. Apart from the prediction at 300 °C, the thermal degradation of cellulose can be evaluated well by the model. When lignin is examined, the relative errors between the predictions and the measurements are always less than 14% (Fig. 13c), stemming from the relatively inactive of lignin in a torrefaction environment. The established kinetics is also able to provide a good prediction on the torrefaction of xylan where the maximum relative error is around 13% (Fig. 13d).

In a previous study [11], it has been outlined that no synergistic effect is exhibited when hemicellulose, cellulose and lignin are co-torrefied. This reflects that the linear superposition of conversion of the three constituents is available when they are torrefied together. In the study of Rousset et al. [22], they have assumed that wood thermal decomposition was a superposition of the thermal degradation of hemicellulose, cellulose and lignin in proportion to their

content in wood. Consequently, the co-torrefaction kinetics of the three constituents with equivalent amount (viz. hemicellulose: cellulose: lignin = 1: 1: 1) is examined in Fig. 14 where the kinetics is defined as

$$X = \frac{1}{3}X_{\text{hemicellulose}} + \frac{1}{3}X_{\text{cellulose}} + \frac{1}{3}X_{\text{lignin}} \quad (9)$$

As a whole, the behavior of co-torrefaction can be predicted accurately, except for at 300 °C. Though the difference between the prediction and the experiment is somewhat pronounced at 300 °C, the trend of conversion is still reasonable. Besides, such a high-temperature is usually not recommended for torrefaction [11]. Consequently, the above observations have clearly pointed out that the developed isothermal kinetics is a feasible tool to account for the torrefaction behavior of biomass once the contents of hemicellulose, cellulose and lignin are known.

5. Conclusions

Thermal decompositions and kinetics of four basic constituents, including hemicellulose, cellulose, lignin and xylan, at five different temperatures (i.e. 200, 225, 250, 275 and 300 °C) with 1h torrefaction have been investigated in the present study. From the distributions of TGA and DTG, it is found that xylan is always sensitive to torrefaction for the temperature range of 200–300 °C. When the torrefaction temperature is not higher than 225 °C, it almost has no influence on hemicellulose, whereas cellulose will be affected if the temperature is as high as 275 °C. In regard to lignin, its thermal degradation is relatively insensitive to torrefaction, regardless of what the temperature is. According to the analyses, it is concluded that biomass with the torrefaction temperatures of 200 and 225 °C pertain to light torrefaction; 250 °C is mild torrefaction, and 275 and 300 °C belong to severe torrefaction. From the conducted kinetics, the appropriate values of order of reaction of hemicellulose, cellulose, lignin and xylan are 3, 1, 1 and 9, respectively, whereas their activation energies are 187.06, 124.42, 37.58 and 67.83 kJ mol⁻¹, respectively. The developed model can predict the thermal decompositions of the materials well, except for cellulose at 300 °C and hemicellulose at 275 °C. With the assumption of no interaction (synergistic effect) among the torrefactions of hemicellulose, cellulose and lignin, the co-torrefaction of the three materials can also be described well by the kinetics. From the application point of view, once the contents of hemicellulose, cellulose and lignin in biomass are identified, the torrefaction process of the biomass can be predicted from the developed model. Therefore, the established kinetics can be employed as a useful tool for designing torrefaction processes in industry.

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References

- [1] Franco A, Diaz AR. The future challenges for "clean coal technologies": Joining efficiency increase and pollutant emission control. *Energy* 2009;34:348–54.
- [2] International Energy Agency. *World Energy Outlook*; 2007.
- [3] Chen WH, Kuo PC. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy* 2010;35:2580–6.
- [4] Chen WH, Wu JS. An evaluation on rice husk and pulverized coal blends using a drop tube furnace and a thermogravimetric analyzer for application to a blast furnace. *Energy* 2009;34:1458–66.
- [5] Ozbay NA, Apaydin-Varol E, Uzun BB, Putun AE. Characterization of bio-oil obtained from fruit pulp pyrolysis. *Energy* 2008;33:1233–40.

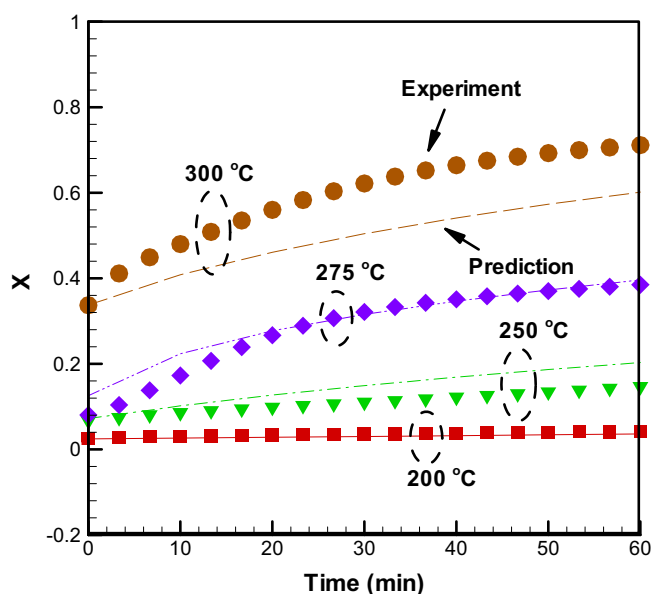


Fig. 14. Comparisons of conversion between predictions and experiments of co-torrefaction at various torrefaction temperatures for 1 h (hemicellulose: cellulose: lignin = 1: 1: 1).

- [6] Singhabhandhu A, Tezuka T. A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock. *Energy* 2010;35:2493–504.
- [7] Chen WH, Tu YJ, Sheen HK. Impact of dilute acid pretreatment on the structure of bagasse for bioethanol production. *International Journal of Energy Research* 2010;34:265–74.
- [8] Clausen LR, Elmegaard B, Houbak N. Technoeconomic analysis of a low CO₂ emission dimethyl ether (DME) plant based on gasification of torrefied biomass. *Energy* 2010;35:4831–42.
- [9] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology* 2011;102:1246–53.
- [10] Chen WH, Kuo PC. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. *Energy* 2011;36:803–11.
- [11] Prins MJ, Ptasiński KJ, Janssen FJJG. Torrefaction of wood. Part 1. Weight loss kinetics. *Journal of Analytical and Applied Pyrolysis* 2006;77:28–34.
- [12] Sadaka S, Negi S. Improvements of biomass physical and thermochemical characteristics via torrefaction process. *Environmental Progress and Sustainable Energy* 2009;28:427–34.
- [13] Felfri FF, Luengo CA, Suarez JA, Beaton PA. Wood briquette torrefaction. *Energy for Sustainable Development* 2005;9:19–22.
- [14] Chaouch M, Pétrissans M, Pétrissans A, Gérardin P. Use of wood elemental composition to predict heat treatment intensity and decay resistance of different softwood and hardwood species. *Polymer Degradation and Stability* 2010;95:2255–9.
- [15] Deng J, Wang GJ, Kuang JH, Zhang YL, Luo YH. Pretreatment of agricultural residues for co-gasification via torrefaction. *Journal of Analytical and Applied Pyrolysis* 2009;86:331–7.
- [16] Yan W, Acharjee TC, Coronella CJ, Vasquez VR. Thermal pretreatment of lignocellulosic biomass. *Environmental Progress and Sustainable Energy* 2009;28:435–40.
- [17] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* 2008;87:844–56.
- [18] Chen WH, Hsu HC, Lu KM, Lee WC, Lin DC. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. *Energy* 2011;36:3012–21.
- [19] Uslu A, Faaij APC, Bergman PCA. Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. *Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation*. *Energy* 2008;33:1206–23.
- [20] Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing Technology* 2008;89:169–75.
- [21] Yan W, Hastings JT, Acharjee CT, Coronella CJ, Vasquez VR. Mass and energy balances of wet torrefaction of lignocellulosic biomass. *Energy Fuels* 2010;24:4738–42.
- [22] Rousset P, Turner I, Donnot A, Perre P. The choice of a low-temperature pyrolysis model at the microscopic level for use in a macroscopic formulation. *Annals of Forest Science* 2006;63:213–29.
- [23] Turner I, Rousset P, Remond R, Perre P. An experimental and theoretical investigation of the thermal pretreatment of wood (*Fagus sylvatica* L.) in the range of 200–260 °C. *International Journal of Heat and Mass Transfer* 2010;53:715–25.
- [24] Repellin V, Govin A, Rolland M, Guyonnet R. Modelling anhydrous weight loss of wood chips during torrefaction in a pilot kiln. *Biomass and Bioenergy* 2010;35:2580–6.
- [25] Galvagno S, Cas S, Martino M, Palma ED, Portofino S. Thermal and kinetic study of tyre waste pyrolysis via TG-FTIR-MS analysis. *Journal of Thermal Analysis and Calorimetry* 2007;88:507–14.
- [26] Murugan P, Mahinpey N, Mani T, Freitag N. Pyrolysis and combustion kinetics of fosterton oil using thermogravimetric analysis. *Fuel* 2009;88:1708–13.
- [27] Khezami L, Chetouani A, Taouk B, Capart R. Production and characterisation of activated carbon from wood components in powder: cellulose, lignin, xylan. *Powder Technology* 2005;157:48–56.
- [28] Sun L, Chen YJ, Negulescu II, Moore MA, Collier BJ. Kinetics modeling of dynamic pyrolysis of bagasse fibers. *Bioresource Technology* 2011;102:1951–8.
- [29] Muller-Hagedorn M, Bockhorn H, Krebs L, Muller U. A comparative kinetic study on the pyrolysis of three different wood species. *Journal of Analytical and Applied Pyrolysis* 2003;68–69:231–49.
- [30] Mui ELK, Cheung WH, Lee VKC, McKay G. Compensation effect during the pyrolysis of tyres and bamboo. *Waste Management* 2010;30:821–30.
- [31] Sonobe T, Worasuwannarak N. Kinetic analyses of biomass pyrolysis using the distributed activation energy model. *Fuel* 2008;87:414–21.
- [32] Yang H, Yan R, Chin T, Tee DL, Chen H, Zheng C. Thermogravimetric analysis-fourier transform infrared analysis of palm oil waste pyrolysis. *Energy Fuels* 2004;18:1814–21.
- [33] Lopez Pasquali CE, Herrera H. Pyrolysis of lignin and IR analysis of residues. *Thermochimica Acta* 1997;293:39–46.
- [34] Varhegyi G, Antal Jr MJ, Jakab E, Szabo P. Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis* 1997;42:73–87.